

#56221 Review

SUMMARY

REVIEW

EDITING

Submission

Authors	Siti Jamilatun, Ilham Mufandi, Arief Budiman, Suhendra Suhendra
Title	Biochar from Slow Catalytic Pyrolysis of Spirulina platensis Residue: Effects of Temperature and Silica-Alumina Catalyst on Yield and Characteristics
Section	Articles
Editor	Dr.-Ing. Teguh Ariyanto, S.T., M.Eng.

Peer Review

Round 1

Review Version	56221-170555-2-RV.DOCX 2020-06-02
Initiated	2020-06-18
Last modified	2020-07-19
Uploaded file	Reviewer B 56221-177277-1-RV.PDF 2020-07-18 Reviewer A 56221-177242-1-RV.DOCX 2020-07-18

Editor Decision

Decision	Accept Submission 2020-09-01
Notify Editor	Editor/Author Email Record 2020-09-01
Editor Version	56221-171608-1-ED.DOCX 2020-06-02
Author Version	56221-180545-1-ED.DOCX 2020-08-16 DELETE 56221-180545-2-ED.DOCX 2020-08-30 DELETE
Upload Author Version	<div>Choose FileNo file chosen</div> <div>Upload</div>

Jurnal Rekayasa Proses (print ISSN 1978-287X; online ISSN 2549-1490) is published by Chemical Engineering Department, Faculty of Engineering, Universitas Gadjah Mada. View website statistics.

ONLINE FIRST ARTICLES

List of articles waiting for an issue number

- Focus and Scope
- Author Guideline
- Online Submission
- The Statement of Originality
- Author Fees
- Publication Ethics
- Visitor Statistics
- Peer Reviewer

Stat Counter 00154146

TEMPLATE



MEMBER OF



CITATION ANALYSIS

SCOPUS

Google Scholar

REFERENCE MANAGEMENT



USER

You are logged in as...

sitijamilatun

- My Journals
- My Profile
- Log Out

AUTHOR

- Submissions
- Active (0)
- Archive (2)
- New Submission

JOURNAL CONTENT

Search

Search Scope

All

Search

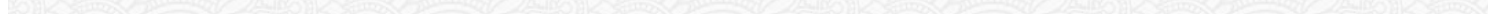
Search

Browse

- ▶ By Issue
- ▶ By Author
- ▶ By Title
- ▶ Other Journals

KEYWORDS

Botryococcus braunii
adsorption **anaerobic**
digestion batik **biogas**
coagulation energy
efficiency fruit waste
glycerol hydrogen kinetics
leaching methane
microalgae natural
coagulant organic fertilizer
precipitation shrinking
core **simulation**
wastewater zeolit



LAMPIRAN 3. SUBMISSION ACKNOLEGMENT

The screenshot displays a Gmail interface on a Windows 10 desktop. The browser window shows the Gmail inbox with a search bar containing 'jurnal.rekpros@ugm.ac.id'. The email list on the left includes 'Kotak Masuk' (9,572), 'Berbintang', 'Ditunda', 'Penting', 'Terkirim', 'Draf' (198), 'Kategori', 'Unwanted', 'Chat', and 'Ruang'. The selected email is titled '[jrekpros] Submission Acknowledgement' from 'Dr.-Ing. Teguh Ariyanto' to 'siti.jamilatun'. The email body contains a thank you message, a manuscript URL, and contact information. The desktop taskbar at the bottom shows various applications and the system clock indicating 18:04 on 06/07/2022.

[jrekpros] Submission Acknowledgement Kotak Masuk x

Dr.-Ing. Teguh Ariyanto <jurnal.rekpros@ugm.ac.id>
kepada saya

Siti Jamilatun:

Thank you for submitting the manuscript, "The influence of Temperature and Silica-alumina Catalyst on Biochar Yield and Characteristics during Slow Pyrolysis of Spirulina Platensis Residue (SPR)" to Jurnal Rekayasa Proses. With the online journal management system that we are using, you will be able to track its progress through the editorial process by logging in to the journal web site:

Manuscript URL: <https://jurnal.ugm.ac.id/jrekpros/author/submission/56221>
Username: siti.jamilatun

If you have any questions, please contact me. Thank you for considering this journal as a venue for your work.

Dr.-Ing. Teguh Ariyanto
Jurnal Rekayasa Proses

Jurnal Rekayasa Proses
<http://journal.ugm.ac.id/index.php/jrekpros>

Noted with thanks. Thanks a lot. Thank you for your response.

Balas Teruskan

The statement of o....pdf The statement of o....pdf A PYROLYSIS OF 8....pdf A PYROLYSIS OF 8....pdf REVIEW DOKUME....pdf Show all x

Type here to search 77°F Clear 18:04 06/07/2022

LAMPIRAN 4. EDITOR DECISION

The screenshot shows a Gmail interface on a desktop. The browser tabs at the top include '[jrekpros] Editor Decision - sitija', 'The statement of originality_S...', 'Manage deposits - Repository', '(278) WhatsApp', 'Sistem Informasi Manajemen P...', 'Download file | iLovePDF', and '#56221 Review'. The address bar shows a Gmail search link for 'jurnal.rekpros%40ugm.ac.id'. The Gmail header shows the search bar with 'jurnal.rekpros@ugm.ac.id' and a profile icon for 'AHMAD DAHLAN'. The left sidebar shows the 'Email' section with categories like 'Kotak Masuk' (9,572), 'Berbintang', 'Ditunda', 'Penting', 'Terakhir', 'Draf' (198), 'Kategori', 'Unwanted', 'Chat' (with contacts like Rachma Tia Evitasari, maryudi maryudi, Melia Dian, Heni Anggorowati, Shinta Amelia, Aous Aktawan), 'Ruang' (Meeting Prodi Teknik KI...), and 'Rapat'. The main content area displays an email from '[jrekpros] Editor Decision' (Kotak Masuk) received on 'Sel, 1 Sep 2020 07.38'. The email body contains the following text:

Dr.-Ing. Teguh Ariyanto, S.T., M.Eng. <teguh.ariyanto@ugm.ac.id>
kepada saya, Ilham, Arief ▾
Siti Jamilatun:

We are pleased to inform you that your recent submission titled, "The influence of Temperature and Silica-alumina Catalyst on Biochar Yield and Characteristics during Slow Pyrolysis of Spirulina Platensis Residue (SPR)", has been accepted for publication in Jurnal Rekayasa Proses.

Please complete the statement of originality as attached and send the filled form to jurnal.rekpros@ugm.ac.id as soon as possible. For publication process, we will contact you again when your proof is ready for you to check before its publication.

You are also requested to pay publication fee
Amount: Rp. 1000.000.- to:
Account name: UGM TKJTKM PUBLIKASI FEE
Bank: Bank Negara Indonesia
Account number: 988881738411851.
Once you make a payment, please send receipt to our administrative staff via: renny.puspita@ugm.ac.id and cc to jurnal.rekpros@ugm.ac.id

and we will further proceed your publication process after receiving your payment.

Thank you for your interest in Jurnal Rekayasa Proses. We look forward to publishing your future article.

Managing Editors,
Dr.-Ing. Teguh Ariyanto, S.T., M.Eng.
Chemical Engineering Department, Universitas Gadjah Mada
teguh.ariyanto@ugm.ac.id

The bottom of the screen shows a Windows taskbar with the search bar, taskbar icons, and system tray showing '77°F Clear' and '18:06 06/07/2022'.



SURAT PERNYATAAN KEASLIAN NASKAH

Saya yang bertanda tangan di bawah ini:

Nama : 1) Siti Jamilatun
2) Ilham Mufandi
3) Arief Budiman
4)

Institusi* : Universitas Ahmad Dahlan

Email* : sitijamilatun@che.uad.ac.id / phone: 081933096313

Tempat, tgl lahir* : Klaten, 12 Agustus 1966.

Alamat* : Jalan Barokah, Gang Nuri 361 Cebongan Kasihan, Ngestiharjo, Bantul, DIY

Judul artikel : **Biochar from Slow Catalytic Pyrolysis of Spirulina platensis residue: Effects of Temperature and Silica-Alumina Catalyst on Yield and Characteristics**

Artikel diterima : tanggal 1(satu) bulan September tahun 2020

Saya menyatakan bahwa artikel tersebut di atas merupakan naskah asli, hasil pemikiran sendiri, bukan saduran/terjemahan, dan belum pernah dipublikasikan di media apapun. Saya bersedia bertanggung jawab jika kelak terdapat pihak tertentu yang merasa dirugikan secara pribadi atau tuntutan hukum atas diterbitkannya artikel ini.

Demikian pernyataan ini saya buat untuk dapat dipergunakan sebagaimana mestinya.

Yogyakarta, 2 September 2020

Penulis,

(Siti Jamilatun)

** Tuliskan data penulis utama*

Pernyataan ini dikirimkan kembali via e-mail: jurnal.rekpros@ugm.ac.id



Biochar from Slow Catalytic Pyrolysis of *Spirulina platensis* Residue: Effects of Temperature and Silica-Alumina Catalyst on Yield and Characteristics

Siti Jamilatun^{1*}, Ilham Mufandi², Arief Budiman³, Suhendra¹

¹Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Jalan Kapas 9, Yogyakarta 55166, Indonesia

²Department of Mechanical Engineering, Faculty of Engineering, Khon Kaen University, Thailand

³Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada Jalan Grafika No. 2, Kampus UGM, Yogyakarta 55281

*Corresponding author: sitijamilatun@che.uad.ac.id

(Submission: 20 May 2020; Revision: 16 August 2020; Acceptance: 1 September 2020)

ABSTRACT

The use of biochar varies on its ability as an adsorbent which adsorbs liquid or gas molecules. Biochar from *Spirulina platensis* residue (SPR) as an energy source, as its richness in nutrients, can be used as fertilizer and maintain water resources in plantations. Biochar can be used as an intermediary for the synthesis of nanotubes, activated carbon, carbon black, and carbon fiber. One of the essential things to be considered in the application of activated carbon from SPR is char's characteristics. This study aimed to obtain data on the biochar and components from the pyrolysis of *Spirulina platensis* residue. The study was conducted in a fixed-bed reactor with electric heaters with a variety of temperatures (300-700 °C) and the amount of silica-alumina catalyst (0-20%). The biochar weight was obtained by weighing the char formed at the end of the pyrolysis. The char characteristics were obtained by the surface area, total pore volume, and pore size analysis. Based on the study results, the relationship between temperature and the amount of catalyst on the characteristics of biochar was studied. The higher the pyrolysis temperature, the less biochar. Also, the use of catalysts can reduce the amount of biochar. The higher the temperature, the higher the surface area and the total pore volume while the pore radius was reduced. The optimum condition for maximum biochar yield in non-catalytic pyrolysis at a temperature of 300 °C was 49.86 wt.%. The surface area, the total pore volume, and the pore radius at 700 °C catalytic pyrolysis with 5% silica-alumina was obtained as 36.91 m²/g, 0.052 cm³/g, and 2.68 nm, respectively.

Keywords: biochar; pore radius; silica-alumina; surface area; total pore volume

ABSTRAK

Penggunaan biochar bervariasi pada kemampuannya sebagai adsorben dalam menyerap molekul cairan atau gas. Biochar dari residu *Spirulina platensis* merupakan sumber energi, karena kaya akan unsur hara, dapat digunakan sebagai pupuk dan pemeliharaan sumber daya air di perkebunan. Biochar dapat juga digunakan sebagai perantara untuk sintesis nanotube, karbon aktif, carbon black, dan serat karbon. Salah satu hal penting yang harus diperhatikan dalam aplikasi karbon aktif dari SPR adalah karakteristik arang. Penelitian ini bertujuan untuk mendapatkan data biochar dan komponen dari pirolisis residu *Spirulina platensis*. Penelitian dilakukan di reaktor fixed-bed dengan pemanas listrik dengan variasi suhu (300-700 °C) dan jumlah katalis silika-alumina (0-20%). Berat biochar diperoleh dengan cara menimbang arang yang terbentuk pada akhir pirolisis. Sedangkan karakteristik arang diperoleh dari analisis luas permukaan, volume pori total, dan ukuran pori. Berdasarkan hasil studi hubungan antara suhu dan jumlah katalis terhadap karakteristik biochar yang telah diteliti, semakin tinggi suhu pirolisis maka biochar semakin sedikit. Selain itu, penggunaan katalis dapat mengurangi jumlah biochar. Sebaliknya, semakin tinggi suhu semakin besar luas permukaan, dan volume pori total serta radius pori-pori semakin berkurang. Kondisi optimum untuk biochar maksimum pada pirolisis non katalitik pada suhu 300 °C adalah 49,86 wt.%. Luas permukaan, total volume pori, dan radius pori pada suhu 700 °C untuk pirolisis katalitik silika-alumina 5% diperoleh masing-masing sebesar 36,91 m²/g, 0,052 cm³/g, dan 2,68 nm.

Kata kunci: biochar; luas permukaan; radius pori; silika-alumina; total volume pori

1. Introduction

Pyrolysis is the most studied thermochemical technology to date and has proven to be one of the best techniques for producing biofuels and biochar from biomass feedstocks (Jamilatun et al., 2019; Li et al., 2016; Tripathi et al., 2016). Biomass sources influence biochar production through pyrolysis, biomass properties (e.g., particle size and moisture content), composition (e.g., cellulose, lignin, and ash content), and process parameters (e.g., temperature, heating rate, residence time) (Yu et al., 2017a). Dickerson and Soria (2013) explained the process parameters for slow pyrolysis; the heating rate is 0.1-1 °C/sec with residence time in the range of minutes to hours, and temperatures between 400-600 °C will produce around 33% char, 32% tar, and 35% gas. The intermediate pyrolysis at 400-500 °C,

a heating rate at 1-1000 °C/sec, hot vapor residence at 10-30 seconds will produce 25% char, 50% tar, and 25% gas. In contrast, fast pyrolysis can provide 12% char, 75% tar, and 13% gas with a heating rate of 10 to more than 1000 °C/sec, a residence time of fewer than 2 seconds, and an optimum temperature between 400-650 °C (Jamilatun et al., 2017; Suganya et al., 2016).

Non-catalytic pyrolysis produces low-quality liquid products with a relatively high oxygenated compound content, which can cause corrosion to the engine. Reduction of oxygenate compounds can improve quality; another way is to use a catalyst during pyrolysis (Jamilatun et al., 2019). One of the catalysts commonly used for cracking hydrocarbons is silica-alumina, the solid acid catalyst most widely used in supporting the production of petrochemicals, chemicals, and renewable energy. High acidity (low Si/Al) can

be used in the process of cracking petroleum; its function is to increase oxidation of CO (Wang et al., 2019). The silica-alumina catalyst is suitable for upgrading bio-oil, has a high melting point (1818 °C) and surface area (Cheng et al., 2016; Duan et al., 2013). The catalytic pyrolysis results can improve bio-oil and biochar; it is essential to know the yield and characteristics (surface area, total pore volume, pore radius) of biochar produced in biochar application.

Microalgae is currently a third-generation raw material for biofuel production. It also produces several pharmacologically necessary and nutritious chemicals such as pigments and fatty acids. The simultaneous production of biofuel raw materials and fine chemicals in microalgae biorefinery can improve the economy (Elkhalifa et al., 2019). Biochar from the pyrolysis of microalgae has a lower surface area and carbon content than biochar from lignocellulose. However, biochar has excellent characteristics such as higher pH, its ability to balance soil acidity, and higher nutrient content, including minerals such as nitrogen, ash, and inorganic elements compared to another biomass. Other characteristics of biochar from microalgae such as surface area, total pore volume, and pore radius are still rarely discussed; for this reason, it is necessary to identify with the BET method (Chen et al., 2018; Ido et al., 2019).

Biochar is a solid residue from pyrolysis, formed from primary and secondary pyrolysis reactions, containing carbon and stable elements with high carbon content. The use of biochar varies because of its inert nature and ability to absorb liquid or gas molecules, as a gasification substrate for energy generation. It has excellent potential to be used directly for combustion because it emits

much lower CO₂ with higher energy than fossil fuels (Lee et al., 2020). Biochar can be used directly as a solid form of biofuel without the complicated extraction process required by liquid-based biofuels. Another advantage of biochar is that the nutrients can be used as fertilizer and to maintain water resources on plantations. As an intermediate material, biochar can be used as a raw material for the synthesis of nanotubes, activated carbon, carbon black, and carbon fiber (Lee et al., 2020).

Biochar with a relatively high surface area can be used as a catalyst and for wastewater treatment. Some biochar from microalgae such as *Chlorella sp.*, *Chlamydomonas sp.*, *Coelastrum sp.*, *Spirulina platensis* has a surface area of 6.163, 2.122, 15.032 and 167 m²/g with pyrolysis time of 0.5, 0.5, 0.5 and 2 hours, respectively (Choi et al., 2020). Wang et al. (2013) reported that the surface area of biochar originating from *Chlorella vulgaris* (2.4 m²/g), macroalgae *Eucheuma sp.* has a much higher surface area (30.03-34.82 m²/g) than other species ranging from 1.29 to 8.87 m²/g (Yu et al., 2017b).

Research on the characteristics of biochar from microalgae and their applications is still not widely found, therefore data on pore area, total pore volume, and pore radius is essential to determine the superiority of biochar from microalgae. This paper aims to study the effect of temperature and the amount of silica-alumina catalysts on product yields and product biochar characteristics from the pyrolysis of residual *Spirulina platensis* (SPR). Biochar characteristics were analyzed by the Brunauer-Emmett-Teller (BET) method and catalysts by the BET method and XRF. The SPR is obtained from solid residue extraction of *Spirulina platensis*. The study was conducted

with fixed bed reactors with a variety of temperatures (400-700 °C), and the amount of silica-alumina catalyst (5-20 %). The catalyst was in the form of pellets. Based on the characteristic data obtained, it is expected that there will be a follow-up treatment from biochar so that it can be appropriately utilized.

2. Research Methodology

2.1 Materials

Dry *Spirulina platensis* residue (SPR) was obtained from *Spirulina platensis* (SP) solid residue extraction, while SP was obtained from Nogotirto Algae Park, Yogyakarta, Indonesia. Wet *Spirulina platensis* residue (SPR) was first sun-dried for three days, then cleaned, and stirred for homogenization. The SPR was stored in a dry and closed place. Then, the SPR was analyzed for the ultimate and proximate content (Jamilatun et al., 2019).

Silica-alumina was obtained in powder form from PT Pertamina Balongan, Indramayu, Indonesia. For applications in pyrolysis, it needs to be formed in the form of pellets. Pellets were created by mixing silica-alumina (95 wt.%) with kaolin (5 wt.%). Distilled water was added to the homogeneous mixture and it was formed into pellets of 4 mm in diameter and 6 mm high. The catalyst pellet was dried in a furnace at 500 °C for 2 hours, then cooled in a desiccator.

2.2 Procedures

Fifty (50) g SPRs were put into the reactor, then tightly closed, and heated with electricity. Temperature controlled with a NiCr-Ni thermocouple placed outside the reactor. Heating was carried out at a heating rate of 5-35 °C/minute from room temperature (30 °C) to the desired

temperature (300-700 °C). Pyrolysis gas was condensed, liquid products coming out of the condenser were collected in the accumulator, and the amount of gas production was measured. Biochar products were obtained after the experiment was completed. The amount of biochar was measured by weighing. The biochar yields were calculated by Equation (1).

2.3 Instrument and data analysis

The experiment was carried out in a fixed-bed reactor made of stainless steel with the inner diameter of 40 mm, the outer width of 44 mm, and the height of 600 mm, equipped with a heater of nickel wire wrapped around the reactor's outer cylinder (Jamilatun et al., 2019). The pyrolysis system's diagram with the fixed-bed reactor is presented in Figure 1.

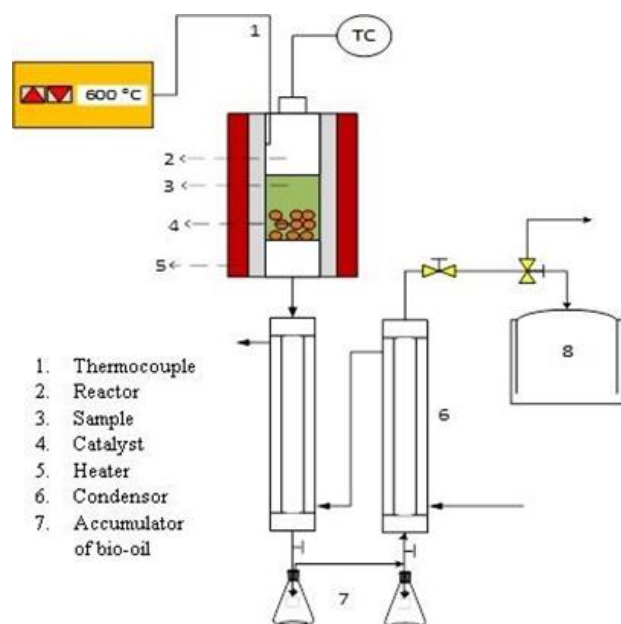


Figure 1. The Pyrolysis system of SPR (Jamilatun et al., 2019)

The reactor is constructed of two cylindrical reactors in vertical series (Reactors 1 and 2). *Spirulina platensis* residue of 50 g is put into the top of reactor one and the catalyst to the bottom of the two reactors,

then tightly closed and heated. The temperature of the reactor was controlled by a NiCr-Ni thermocouple that was placed outside of the reactor. The SPR samples were heated with a heating rate in the range of 5-35 °C/min from 30 °C to the desired temperature range of 300-700 °C. The condenser unit condensed the pyrolysis gas. The liquid yield was collected in the accumulator, and the produced gas was measured. After the experiment finished, the remaining solid product (biochar) was taken and weighed. The bio-oil yields were calculated by Equation 1.

2.3.1 Biochar Yield

The biochar yield was calculated using Equation (1).

$$Y_C = \frac{W_C}{W_M} \times 100\% \quad (1)$$

In this case, Y_C notation is the yield of charcoal products, while W_M and W_C are the initial SPR weighting and charcoal weight, respectively.

2.3.2 Sample of *Spirulina platensis* residue

Spirulina platensis residue sample analysis included proximate, ultimate, and higher heating value (HHV). Proximate analysis (protein with the Kjeldahl method; carbohydrates with the Anthrone method; lipids with the Soxhlet method) and HHV (Bomb calorimeter) were carried out at the Laboratorium Pangan dan Hasil Pertanian, Departemen Teknologi Pertanian dan Laboratorium Pangan dan Gizi, Pusat Antar Universitas (PAU), UGM Indonesia. The ultimate analysis (C, H, O, N, and S with a standard D 2361) was conducted at the Laboratorium Pengujian, Puslitbang Tekmira, Bandung Indonesia.

2.3.3 Silica-Alumina

Measurement of the surface area, total pore volume, and radius pore were carried out using the BET method (Brunaur, Emmett, and Teller) by Quantachrome NovaWin - Data Acquisition and Reduction NOVA instruments 1994-2013, Quantachrome Instruments version 11.03. The content of C, O, Al, Si, and silica-alumina ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ with SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray), each conducted at the Laboratorium Penelitian dan Pengujian Terpadu (LPPT), UGM. (Jamilatun et al., 2019). The X-ray fluorescence (XRF) analysis was carried out at The International Frontier Division, Dept. Transdisciplinary Science and Technology School of Environmental and Society, Tokyo Institute of Technology, Japan. The XRF microscopy analyzes were carried out at normal atmospheric pressure with currents of 50 kV and 1.0 mA, in the Horiba Scientific XGT-5200 Analytical X-ray Microscope, with high spatial resolution from 1.2 mm to 10 μm .

2.3.4 Biochar Product

Prior to the adsorption test, biochar was degraded at 150 °C for 10 hours. The specific surface area of BET (S_{BET}) was determined by the Brunauer-Emmett-Teller equation (BET). Total pore volume (V_{total}) was established by a single point adsorption total pore volume analysis. The $4V/S_{\text{BET}}$ determines the average pore diameter (D) based on the BET method (Chen et al., 2018). BET analysis was carried out at the Laboratorium Analisis Instrumental (ANINS), Chemical Engineering Department, UGM by Quantachrome Nova Win-Data Acquisition and Reduction for NOVA instruments 1994-2013, Quantachrome Instruments version 11.03.

3. Results and Discussions

3.1 Analysis Results

The SPR sample ultimate analysis revealed the percentage of C, H, N, and O of 41.36, 6.60, 7.17, and 35.33 wt.%, respectively. On the other hand, the proximate analysis resulted in the lipids, proteins, and carbohydrates composition of 0.09, 49.60, and 38.51 wt.%, respectively. While the HHV of the SPR is 12.8 MJ/kg.

Silica-alumina was analyzed by Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). The results are shown in Figure 2.

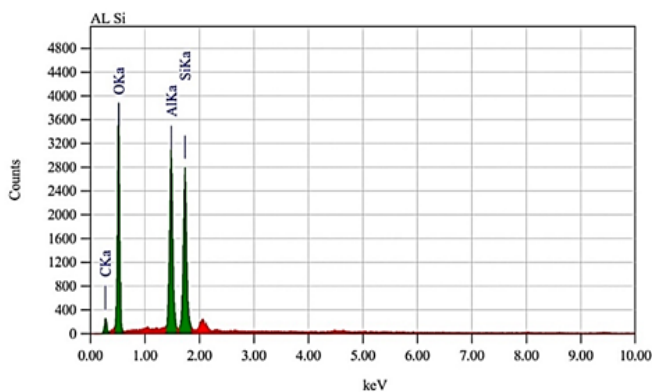


Figure 2. Silica-alumina SEM-EDX results

Figure 2 shows the magnitude of the voltage (keV) used, and each catalyst constituent (C, O, Al, and Si). Si obtained at a voltage of 1.739 keV with a complete counting of 2400 counts, while Al is received at a voltage of 1.486 keV with 6800 counts. Based on the ZAF Standardless Quantitative Analysis Method and using the Fitting Coefficient: 0.0684, the weight percent values of C, O, Al, and Si were 12.33, 55.73, 15.42, and 16.51%, respectively. Meanwhile, from the BET measurement, surface area, average pore volume, and pore diameters were 240.53 m²/g, 0.199 cm³/g total pore volume, and 3.3 nm. The XRF analysis results of SiO₂, Al₂O₃, and ratio SiO₂/Al₂O₃ were 60.28 wt., 35.25 wt.,

and 1.71%, respectively (Jamilatun et al., 2019).

3.2 Biochar Yield

The biochar yield data of pyrolysis with fixed-bed reactors at various temperatures and the amount of silica-alumina is shown in Figure 3

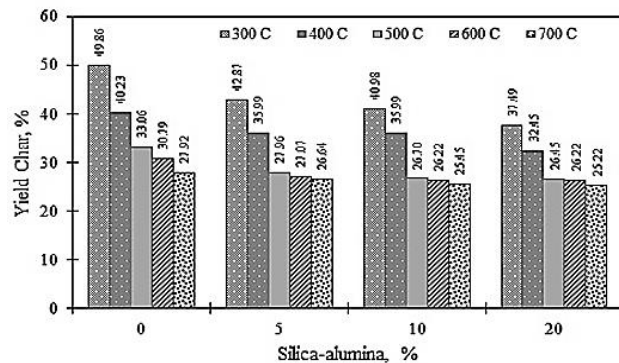


Figure 3. The influence on temperature and amount of catalyst on biochar yield

Based on Figure 3, the pyrolysis temperature rise of non-catalytic and catalytic pyrolysis has a similar trend. The increasing pyrolysis temperature will affect the biochar yield to decrease further. The increase in pyrolysis temperature will reduce the biochar yield. It causes thermal cracking of the heavy hydrocarbon material, leading to an increase in fluids and gases and a decrease in the biochar yield. The primary pyrolysis reaction happens at low temperature, and decomposition occurs gradually to produce charcoal. While at high temperatures, rapid evaporation occurs, which leads to the formation of volatiles. The high temperature causes a secondary pyrolysis reaction. The biochar formed during the primary reaction is decomposed into liquefied and non-condensed gas, reducing the charcoal (Tripathi et al., 2016). In non-catalytic pyrolysis, temperature increases from 300,

400, 500, 600, and 700 °C will produce biochar of 49.86, 40.23, 33.06, 30.79, and 27.92%, respectively.

The addition of silica-alumina to pyrolysis will increase secondary reactions, causing a slight decrease in biochar. In the secondary reaction, the tar will undergo further decomposition into gas to increase the amount of non-condensable gas yield and reduce the amount of condensable-gas and biochar yield. At the temperatures of 300 and 400 °C, the increasing amount of catalyst has little effect on yield decreasing of biochar. Whereas at 500-700 °C, the use of catalysts (5, 10, and 20%) had no impact on reducing the charcoal amount. The optimum conditions of pyrolysis to produce high biochar yield is achieved at a temperature of 300 °C without a catalyst. However, to produce biochar with better characteristics (surface area, total pore volume, and pore radius), a catalyst is recommended.

3.3 Biochar Surface Area

The effect of temperature and the amount of silica-alumina on the biochar surface area is shown in Figure 4. Based on Figure 4, the impact of temperature rise for both non-catalytic and catalytic pyrolysis is quite significant on the surface area. As the temperature gets higher, the surface area tends to increase. The optimum condition is obtained at 700 °C for non-catalytic, the biochar surface area is 23.45 cm²/g, while for catalytic pyrolysis (5% silica-alumina) the surface area is 36.91 m²/g. The biochar surface area for the use of 5% silica-alumina at 400, 500, 600, and 700 °C was 3.99, 4.18, 23.45, and 36.91 m²/g, respectively.

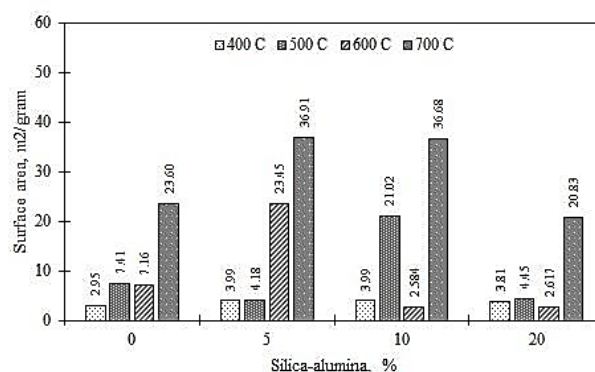


Figure 4. The influence of silica-alumina catalyst on surface area biochar

Microalgae-based biochar appears to be promising in terms of energy potential because of its higher HHV range (14.50-36.67 MJ/kg) and relatively higher surface area (up to 80 m²/g). The content of various functional groups and inorganic elements in biochar is useful in the process of adsorption for environmental control (Lee et al., 2020). Based on the surface area data obtained, it can be interpreted that biochar from microalgae has the potential to be developed into activated charcoal with physical or chemical activation to achieve a larger size of the surface area. The choice of pyrolysis temperature needs to be considered to obtain high biochar yield and surface area. According to Zheng et al. (2017), the pyrolysis of *Chlorella sp.* at a temperature of 600 °C produces biochar with a surface area of 6.16 m²/g. Wang et al. (2013) reported that the biochar surface area of *C. Vulgaris* was 2.40 m²/g, while Roberts et al. (2015) reported on biochar produced from macroalgae *Eucheuma sp.* has a much higher surface area (30.03-34.82 m²/g) than other species ranging from 1.29 to 8.87 m²/g. Compared to this study, the biochar produced by SPR pyrolysis with silica-alumina at the same temperature, namely 600 °C, has a much higher surface area, namely 36.91 m²/g.

3.4 Biochar Total Pore Volume

The effect of temperature and the amount of silica-alumina on the total pore volume are shown in Figure 5. The temperature and the amount of catalyst have significant effects on the total pore volume at 700 °C. The optimum total pore volumes were obtained at a temperature of 700 °C in non-catalytic and catalytic pyrolysis with 5, 10, and 20 % silica-alumina were 0.036, 0.052, 0.052, and 0.041 cm³/g, respectively. The total pore volume data of biochar from microalgae are not published as much as the data for the pore area. However, Chen et al. (2018) report that the pyrolysis of *Spirulina platensis* at 600 °C with a barium (Ba) catalyst produces a total pore volume of 0.004 cm³/g.

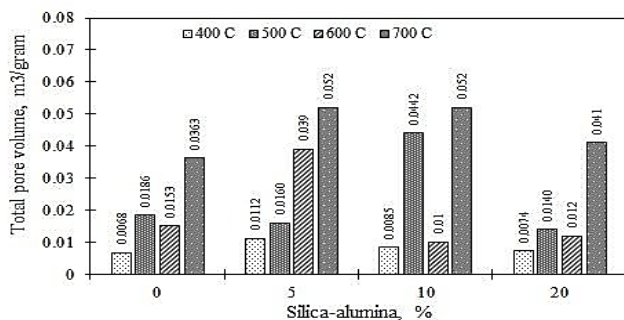


Figure 5. The influence of temperature and the amount of silica-alumina catalyst on total pore volume

3.5 Biochar Pore Size

The effect of temperature and the amount of alumina-silica catalyst on the biochar radius can be seen in Figure 6. Based on this figure, the pore radius for temperatures of 300-400 °C from non-catalytic and catalytic pyrolysis has the same trend. The rising temperature will increase the pore radius, but at a temperature of 700 °C, the pore radius drops sharply. The correlation between surface area and pore radius is that the higher temperature increases the surface area;

otherwise, the pore radius will decrease (Yu et al., 2017b). The pore radius ranges resulted from 400-700 °C for non-catalytic and catalytic pyrolysis with 5%, 10%, and 20% silica-alumina were 2.68-2.70, 2.68-2.72, 2.69-2.71 and 2.68-2.70 nm. The biochar product from non-catalytic and catalytic pyrolysis SPR leads to mesoporous sizes of 2-50 nm. Chen et al. (2018) reported that the biochar product of *Spirulina platensis* from catalytic pyrolysis with Barium (Ba) has the characteristics of pore area, total pore volume, and pore radius of 0.09 m²/g, 0.04 m³/g, and 177 nm, respectively.

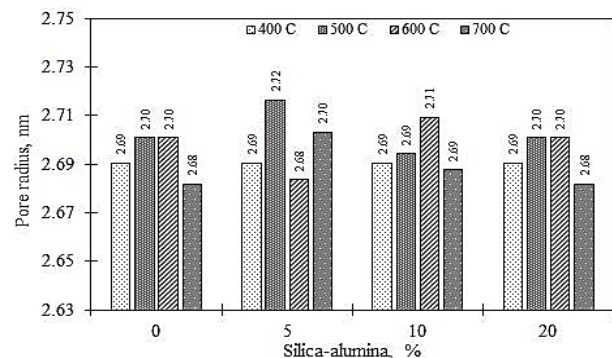


Figure 6. The influence of temperature and the amount of silica-alumina catalyst on pore radius biochar

3.6 Comparison of SPR Biochar Characteristics with the Other Findings

Table 1 compares the process of pyrolysis of different microalgae and the biochar products produced in fixed-bed reactors with slow pyrolysis. The pyrolysis of brown macroalga *Laminaria japonica* and green macroalgae *Cladophora glomerata* shows that the higher the pyrolysis temperature, the lower the yield of biochar (Jung et al., 2016), while the surface area is increasing (Bordoloi et al., 2016; Norouzi et al., 2016). Bordoloi et al. (2016) reported that an increase in temperature from 300-600 °C affected the increase in surface area from 1.72 to 123 m²/g.

Table 1. The pyrolysis process and characteristic biochar microalgae (Yu et al., 2017)

Pyrolysis Process	Biomass feedstock	Temperature (°C)	Biochar production	References
Slow pyrolysis	<i>Brown Laminaria japonica</i> macroalgae	200–800	<ul style="list-style-type: none"> • 78.34% at 200 °C • 63.64% at 400 °C • 37.96% at 600 °C • 27.05% at 800 °C 	Jung et al. (2016)
Fixed-bed pyrolysis	<i>Scenedesmus dimorphus</i>	300–600	Surface area of <i>biochar</i> increased from 1.72 to 123 m ² /g when temperature increased from 300-500 °C; reduced to 89 m ² /g at 600 °C	Bordoloi et al. (2016)
Fixed-bed pyrolysis	Green macroalgae <i>Cladophora glomerata</i>	400–600	<ul style="list-style-type: none"> • 44 wt% yield at 400 °C • 40 wt% yield at 500 °C • 39 wt% yield at 600 °C 	Norouzi et al. (2016)
Fixed-bed pyrolysis Slow pyrolysis	<i>Spirulina platensis</i> residue	300-700	<ul style="list-style-type: none"> • Yield <i>biochar</i> at catalyst 0, 5, 10 and 20 % in the range 27.92-49.86, 26.64-42.87, 25.45-40.98, and 25.22-37.49 %, respectively. • Catalyst 0, 5, 10 and 20 % (700 °C) surface area of 31.47, 36.905, 36.667, 20.826 m²/g, respectively • Catalysts with 0, 5, 10, and 20% (700 °C) total pore volume of 0.036, 0.052, 0.052 and 0.041cm³/g, respectively • Catalysts with 0, 5, 10, and 20 % (700 °C) pore radius of 2.682-2.701, 2.684-2.717, 2.688-2.709 and 2.682-2.701 nm, respectively 	This experiment

The results of non-catalytic and catalytic SPR pyrolysis research at the temperatures of 300-700 °C with the variations of 0, 5, 10, and 20% alumina-silica catalysts yielded biochar yields in the range of 27.92-49.86, 26.64-42.8, 25.45 -40,98, and 25.22-37.49%, respectively.

Based on the yield of biochar, the optimum conditions in non-catalytic pyrolysis were obtained, at a temperature of 300 °C with 49.86 wt.% yield. Based on the characteristics of biochar, the optimum conditions for catalytic pyrolysis was obtained with 5% silica-alumina catalyst at 700 °C, which resulted in the surface area, total pore volume, and pore radius of 36.91 m²/g, 0.052 m³/g, 2.68 nm, respectively.

4. Conclusions

Non-catalytic pyrolysis produces bio-oil with a high content of oxygenated

compounds, so the use of silica-alumina catalysts improves the bio-oil quality. Catalytic pyrolysis will affect the quality of biochar, such as surface area, total pore volume, and pore radius. Non-catalytic and catalytic pyrolysis of *Spirulina platensis* residue (SPR) was carried out in a fixed bed reactor. The results of pyrolysis at the temperatures of 300, 400, 500, 600 and 700 °C with silica-alumina catalyst varied at 0, 5, 10 and 20% were biochar yields in the range of 27.92-49.86, 26.64-42.87, 25.45-40.98 and 25.22-37.49%; the surface area in the range of 2.95-23,60, 3.99-36.91, 3.99-20.83; the total pore volume in the range of 0.007-0.036, 0.011-0.052, 0.009-0.052 and 0.007-0.041 m³/g; and the pore radius in the range of 2.682-2.701, 2.684-2.717, 2.688-2.709 and 2.682-2.701 nm, respectively. The optimum condition for producing the maximum

biochar yield is non-catalytic pyrolysis at the temperature of 300 °C, which is 49.86 wt.%. However, to obtain better biochar characteristics, this condition does not apply. Based on the biochar characteristics, the optimum conditions were obtained at 700 °C by catalytic pyrolysis with 5 % of silica-alumina, which obtained the surface area, total pore volume, and radius pore as 36.91 m²/g, 0.052 m³/g, 2.68 nm, respectively.

Acknowledgements

The researcher would like to thank the internal research funding assistance through the Institute of Research and Community Service (LPPM) Ahmad Dahlan University Yogyakarta with a contract number: PD-237/SP3/LPPM-UAD/2020.

References

- Bordoloi, N., Narzari, R., Sut, D., Saikia, R., Chutia, R.S., and Kataki, R., 2016, Characterization of bio-oil and its sub-fractions from pyrolysis of *Scenedesmus dimorphus*, *Renewable Energy*, 98, 245-253
- Chen, W., K., Xia, M., Yang, H., Chen, Y., X., and Che, Q., 2018, Hanping Chen, Catalytic deoxygenation co-pyrolysis of bamboo wastes and microalgae with biochar catalyst, *Energy*, 157, 472-482.
- Cheng, S., Wei, L., Zhao, X. and Julson, J., 2016, application, deactivation, and regeneration of heterogeneous catalysts in bio-oil upgrading, *Catalysts*, 6, 195.
- Choi, Y-K., Choi, T-R., Gurav, R., Bhatia, S.K., Park, Y-L., Kim, H.J., Kan, E., and Yang, Y-H., 2020, Adsorption behavior of tetracycline onto *Spirulina sp.* (microalgae)-derived biochars produced at different temperatures, *Science of the Total Environment*, 710, 136-282.
- Dickerson, T. and Soria, J., 2013, Catalytic fast pyrolysis: A Review, *Energy*, 6, 514-538.
- Duan, P., Bai, X., Xu, Y., Zhang, A., Wang, F., Zhang, L., and Miao, J., 2013, Catalytic upgrading of crude algal oil using platinum/gamma alumina in supercritical water, *Fuel*, 109, 225-233.
- Elkhalifa, S., Al-Ansari, T., Hamish R. Mackey, and Gordon McKay, 2019, Food waste to biochars through pyrolysis: A review, *Resour., Conserv. Recycl.*, 144, 310-320.
- Ido, AL, de Luna, M.D.G., Ong, D.C., and Capareda, S.C., 2019, Upgrading of *Scenedesmus obliquus* oil to high-quality liquid-phase biofuel by nickel-impregnated biochar catalyst, *J. Cleaner Prod.*, 209, 1052-1060.
- Jung, K.-W., Jeong, T.-U., Kang, H.-J., and Ahn, K.-H., 2016, Characteristics of biochar derived from marine macroalgae and fabrication of granular biochar by entrapment in calcium-alginate beads for phosphate removal from aqueous solution, *Bioresour. Technol.*, 211, 108-116.
- Jamilatun, S., Budhijanto, Rochmadi, and Budiman, A., 2017, Thermal decomposition and kinetic studies of pyrolysis of *Spirulina platensis* residue, *International Journal of Renewable Energy Development*, 6(3), 193-201.
- Jamilatun, S., Budiman, A., Anggorowati, H. Yuliestyan, A., Surya Pradana, Y. Budhijanto, and Rochmadi, 2019, Ex-situ catalytic upgrading of *Spirulina platensis* residue oil using silica-alumina catalyst, *Int. J. Renew. Energy Res.*, 9 (4), 1733-1740.
- Li, J., Dai, J., Liu, G., Zhang, H, Gao, Z., Fu, J., Y., and Huang, Y., 2016, Biochar from

- microwave pyrolysis of biomass: A review, *Biomass Bioenergy*, 94, 228-244.
- Lee, X.J., Ong, H.J., Gan, Y.Y., Chen, W-H., and Mahlia, T.M.I., 2020, State of art review on conventional and advanced pyrolysis of macroalgae T and microalgae for biochar, bio-oil and bio-syngas production, *Energy Convers. Manage.*, 210, 112707.
- Norouzi, O., Jafarian, S., Safari, F., Tavasoli, A., and Nejati, B., 2016, Promotion of hydrogen-rich gas and phenolic-rich bio-oil production from green macroalgae *Cladophora glomerata* via pyrolysis over its bio-char, *Bioresour. Technol.*, 219, 643–651.
- Roberts, D.A., Paul, N.A., Bird, M.I., and de Nys, R., 2015, Bioremediation for coal-fired power stations using macroalgae, *J. Environ. Manage.*, 153, 25–32.
- Suganya, T., Varman, M., Masjuki, H.H., and Renganathan, S., 2016, Macroalgae and microalgae as a potential source for commercial applications along with biofuels production: A biorefinery approach, *Renewable and Sustainable Energy Rev.*, 55, 909–941, 2016.
- Tripathi, M., Sahu, J.N., and Ganesan, P., 2016, effect of process parameters on production of biochar from biomass waste through pyrolysis: A review, *Renewable and Sustainable Energy Rev.*, 55, 467–481.
- Wang, K., Brown, R., C., Homsy S., Martinez, L., and Sidhu S., S., 2013, Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production, *Bioresour. Technol.* 127, 494–499.
- Yu, K.L., Show, P.L., Ong, H.C., T.C., Lan, J.C-W., Chen, W.H., and Chang, J-S., 2017a, Microalgae from wastewater treatment to biochar – Feedstock preparation MARK and conversion technologies, *Energy Convers. Manage.*, 150, 1–13.
- Yu, KL, BF, P.L., Ong, H.C., TC, W-H., Ng, and EP, J-S., 2017b, Recent developments on algal biochar production and characterization, *Bioresour. Technol.*, 246, 2–11.
- Zheng, H., Guo, W., Li, S., Chen, Y., Wu, Q., Feng, X., Yin, R., Ho, S-H., Ren, N., and Chang, J.-S., 2017, adsorption of p-nitrophenols (PNP) on microalgal biochar: analysis of high adsorption capacity and mechanism, *Bioresour. Technol.*, 244, 1456–1464.
-